

## TOTAL VALORISATION OF RED CEDAR (*THUJA PLICATA*) SAWMILLS WASTES. ISOLATION OF EXTRACTIVES AND PRODUCTION OF ACTIVATED CARBON FROM THE SOLID RESIDUE

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Experiments were performed to evaluate a recent extraction process called the instantaneous controlled pressure drop process (briefly: DIC process: “Détente Instantanée Contrôlée”) for extracting some volatile compounds from red cedar wood. This process involves subjecting red cedar chips for a short time (30 s to 5 min) under a steam pressure (1 to 6 bars or from 100 to 165 °C). This first step is followed by a flash decompression toward vacuum (up to 50 mbar). This transition induces a fast evaporation of water and volatile compounds and a cooling effect. The effects of two processing parameters (steam pressure and heating time) on the total extraction yield and on yield of four volatile compounds were evaluated by response surface methodology. The results indicated that the processing pressure is the predominant parameter for global extraction yield of oil (E.O= Extracted Oil) and for yield of the four compounds investigated in this study. The processing time is also a significant parameter but less than processing pressure. Moreover, activated carbon produced from DIC-treated residue revealed larger pore sizes compared to untreated samples.

*Keywords:* Instantaneous controlled pressure drop (DIC Process); Isolation; Extractives; Red cedar (*Thuja plicata*); Volatiles; Wood; Hydrotreatment; Activated carbon

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### INTRODUCTION

In the last decade there has been an increasing demand for new extraction techniques enabling automation, shorter extraction time, and reduced consumption of organic solvent. The Instantaneous Controlled Pressure Drop process, abbreviated DIC according to the French expression “Détente Instantanée Contrôlée”, belongs to these techniques. It was developed and patented by Allaf et al. (2000). DIC extraction is based on a thermo-mechanical processing. It could be also designed as a high temperature-short time process using steam. In this process, a product is subjected in a first step to high temperature and high steam pressure, and this step is followed by a rapid transition towards vacuum. The drop in pressure is termed as instantaneous since the value of  $\Delta P/\Delta t$  is higher than 5 bar.sec<sup>-1</sup>. The exposure of the product to higher temperatures is very

short, and the rapid cooling induced by the rapid decompression towards vacuum allows stopping of further thermal degradation of oil components. It is generally accepted that a long time at high temperatures can cause some rearrangement or polymerisation of the components of extracted oil (Spiro and Chen 1994)

The DIC process was successfully applied for the drying and texturization of food products as fruits and vegetables (Nouviaire et al. 2001) or for improving hydration capacity of polysaccharides (Jeannin et al. 2000). Recently, DIC was used for extracting volatile compounds and essential oils from rosemary leaves (Rezzoug et al. 2005) and from by-products of orange peel (Rezzoug et al. 2000). Moreover, Emmel et al. (2003) cited several advantages associated with steam explosion, amongst which is producing a high yields of specific chemicals from a wide variety of lignocellulosic biomass.

In the present work, the first part is devoted to extraction of volatiles from red cedar (*Thuja plicata*) sawdust by the DIC process. The processing parameters, pressure, and treatment time are optimized to get the highest yield and the best quality of extractives. The optimization is focused on the production of four compounds: carvacrol (C<sub>10</sub>H<sub>14</sub>O), plicatic acid (C<sub>20</sub>H<sub>22</sub>O<sub>10</sub>), 3-isopropylphenol (C<sub>9</sub>H<sub>12</sub>O), and myrtenol (C<sub>10</sub>H<sub>16</sub>O). Indeed, it is well known that oil isolated from red cedar wood contains compounds of high value such as carvacrol, which is commonly used in the food industry, in aromatherapy, and as a therapeutic agent (Lee et al. 2005). Ultee and Smid (2001) argued on the positive influence of carvacrol on inhibition of toxin production by *Bacillus cereus* and then on the safety of food products. More recently, Rajkovic et al. (2005) showed that this compound is an efficient antimicrobial agent. 3-isopropylphenol is used as a germicide, medicinal disinfectant, or solvent for cleaning and dissolution (Fung and Long 2001). Myrtenol is a precursor of various medicinal and aromatic compounds used in the food industry (Milos and Radonic 2000). Plicatic acid was also identified as the primary irritant in cedar in a number of studies (Cartier et al. 1986; Chan-Yeung 1986). This compound was found to be responsible for certain human respiratory symptoms such as asthma (Chan-Yeung 1994). For these reasons, it may be important to remove this compound from red cedar wood before its utilization as a building material.

The second part of this work deals with the quality of activated carbon (A.C.) produced from the residual wood after DIC treatment. In fact, activated carbon is by far the most used sorption material for de-polluting gaseous or liquid effluents. It is often produced from precursors such as wood or various lignocelluloses wastes (coconut shell, fruit stones, etc.). Producing activated carbon requires heating a carbon-rich material up to a temperature in the range 600-1000 °C with an activating agent. The activating agent can be either a stream of CO<sub>2</sub> or H<sub>2</sub>O (steam) in the so-called physical activation or a mineral acid (H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>), a base (KOH), or a salt (ZnCl<sub>2</sub>) in the so-called chemical activation. In the literature nothing is reported for activated carbon produced from wood that was previously subjected to a sudden pressure drop, as in the present study. The only tested thermo-mechanical pre-treatment of wood before activation is the thermo-compression consisting of compacting wood by using a hydraulic press with heating plates. According to Abe et al. (2001) and to Khezami et al. (2007), the previous thermo-compression does not significantly change the microporosity and the adsorption capacity of the final activated carbon. The main advantage rather lies in the higher density of the

final pellets of activated char. In the present study two samples (untreated and DIC-treated wood) were analysed and compared according to the pore sizes obtained after pyrolysis and production of activated carbon.

## EXPERIMENTAL

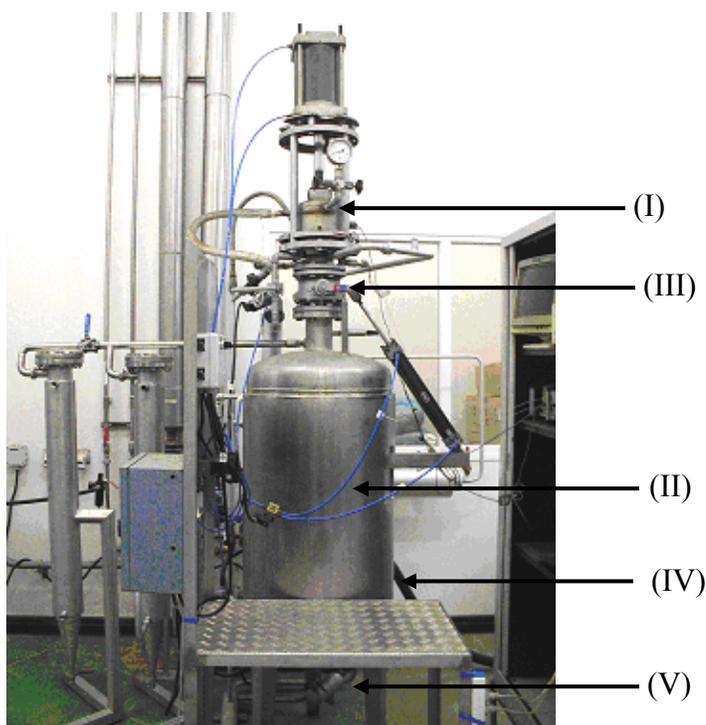
### Raw Material

Pieces of western Red Cedar wood (British Columbia, Canada) were cut in fine chips of 0.5 mm in thickness, and by drying in ambient air their moisture content was reduced to a mean value of 6.6 % on a dry basis.

### Experimental Set-up

The experimental set-up (Fig. 1) is largely described in a previous study (Mellouk, 2007). It is composed of three main elements:

- The processing vessel (I) which contains the wood chips to treat
- The vacuum system which mainly consists in a vacuum tank (II) and a vacuum pump (IV). The capacity of the vacuum tank (360 l) is 30 fold larger than that of the processing vessel (12 l). The initial pressure in the vacuum container was fixed at 50 mbar in all the experiments.



**Fig. 1.** Experimental apparatus for extraction used for oil isolation from red cedar wood by Instantaneous Controlled Pressure Drop. I. Treatment vessel (made of stainless steel); II. Vacuum container; III. Valve; IV. to vacuum pump; V. Extract container.

- A pneumatic valve (III) placed between the processing vessel and the vacuum tank. The opening time of the valve is very short, less than 0.2 s, thus involving a rapid decompression within the reactor.

### Protocol of Extraction by the Instantaneous Controlled Pressure Drop Process

Wood chips are initially placed in the D.I.C vessel (I) and the pressure inside is reduced to 50 mbar (Figure 2b). This partial vacuum allows a better diffusion of steam within the wood so that the time to reach the desired processing pressure (or processing temperature) is shortened. The electropneumatic valve (III) between the reactor and the vacuum tank (II), is then closed, and the DIC reactor is filled with steam up to a processing pressure, the value of which can be fixed from 1 to 6 bar (Fig. 2c). After a certain time at a fixed processing pressure (Fig. 2d), the pneumatic valve is instantaneously opened thus resulting in a rapid pressure drop within the DIC reactor (Fig. 2e). The mixture of condensed steam and extracted volatiles is recovered in a specific vessel placed under the vacuum tank (Fig. 1.V). The volume of the recovered liquid mixture was about 400 ml for all experiments.

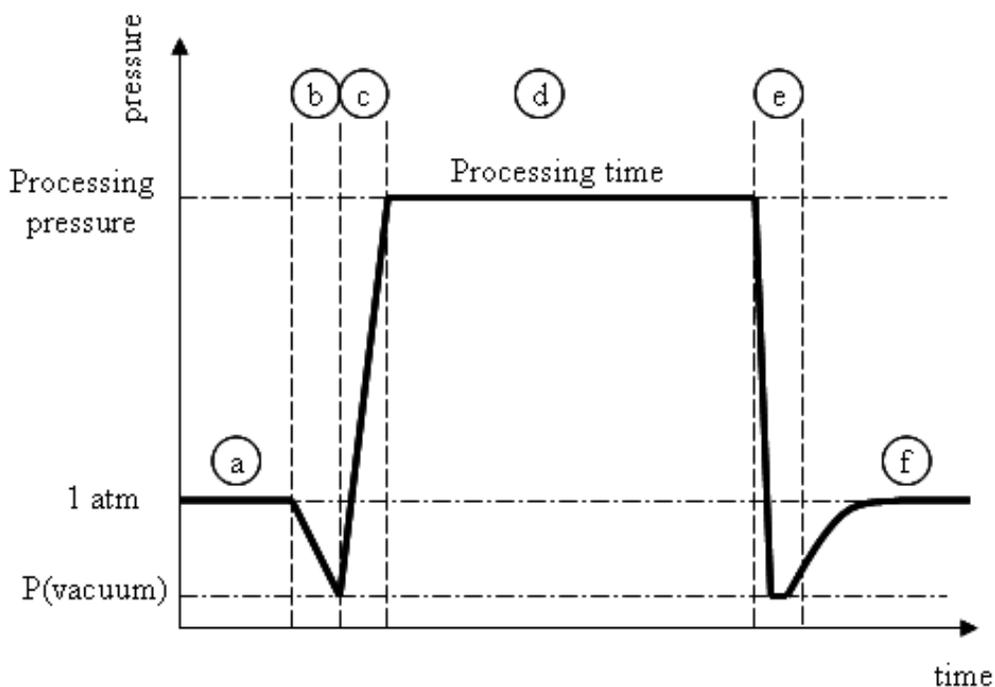


Fig. 2: Typical pressure-time profile for DIC processing cycle.

### Preparation of Activated Carbon

The used activating agent is a concentrated solution of  $H_3PO_4$  (84%). With this agent, the wood is subjected to a certain swelling and to hydrolytic scission reactions of glycosidic bonds, thus enhancing the formation of micro and meso-pores during the heating period. The precursor material, untreated wood or DIC-treated wood, is firstly impregnated with the  $H_3PO_4$  solution at a mass-ratio acid/precursor of 0.25. The

impregnated wood is then dried in a ventilated oven at 70 °C until total evaporation of the free-water. In the subsequent activation step, the impregnated wood is brought to a temperature of 700°C in a tubular oven, under a N<sub>2</sub> stream, at a heating rate of 3°C/min. The maximal temperature of 700 °C is kept constant for 2 hours. Then, the activated carbon (A.C.), after cooling, is treated with a solution of NaOH (0.1 M) up to a neutral pH and abundantly rinsed with some distilled water in order to remove the salt encrustations within the pores. The A.C. is finally dried at 110°C and stored in hermetic container for further analysis. Micromeritics ASAP 2010 equipment was used for the determination of adsorption isotherms.

### GC/MS Conditions

The analyses are performed by using a Varian 3900 gas chromatograph coupled to a Varian Saturn 2100T ion trap mass spectrometer (Varian, France) for characterizing the extracts. The chromatographic column is a 30m×0.25 mm, 0.25 µm CP-Sil 8 CB Low Bleed MS capillary column (Varian, France). The column temperature is 80°C (3min) - 3°C/min - 250°C (40 min) with helium as carrier gas at 1 ml/min. The extract samples are injected via a Varian CP-8400 autosampler fitted with a 5µl syringe. The temperature of transfer line was 280°C. Electron impact mass spectra are obtained at 70 eV ionization potential, and peaks are identified from the data library NIST 2002.

### Steam Distillation

In experiments of steam distillation, a quantity of 2.5 g of wood chips is placed on stainless steel grid and continuously swept during 2 hours by steam produced from a flask of boiling water, at atmospheric pressure. The mixture of steam and extracted volatiles is cooled and condensed after flowing through a cooling coil. An organic phase rich in extracted oil is finally separated from aqueous phase by decantation.

### Experimental Design

The relationships between response functions and process variables have been established by using a 3<sup>2</sup> full-factorial design as well as the optimal conditions of the developed process. Three central points are added in the factorial design to estimate the experimental error and to prove the suitability of the model. The two independent variables are coded according to the following equation:

$$x_i = \frac{X_i - X_{i0}}{\Delta X_i} \quad i = 1,2 \quad (1)$$

where  $x_i$  and  $X_i$  are respectively the dimensionless and the actual values of the independent variable  $i$ ,  $X_{i0}$  the actual value of the independent variable  $i$  at the central point, and  $\Delta X_i$  the step change of  $X_i$  corresponding to a unit variation of the dimensionless value.

The processing pressure (p) and processing time (t) are chosen as independent variables. The selected responses in the experimental design are the total yield in extracted oil and the yield in the four chosen compounds the interest that were discussed in the introduction: plicatic acid, 3-isopropylphenol, carvacrol and myrtenol. Both the coded and actual values of the independent variables are listed in Table 1.

**Table 1.** Experimental Values and Coded Levels of the Independent Variables used for the 3<sup>2</sup> Full-Factorial Design

Independent variable	Variable type, symbol and unit	Levels		
		-1	0	+1
X <sub>1</sub>	Pressure, p (bar)	1	3.5	6
X <sub>2</sub>	Time, t (s)	30	165	300

The 5 various responses Y are related to the coded independent variables  $x_i, x_j$  according to the second order polynomial expressed in the right hand term of equation 2,

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \quad (2)$$

with  $\beta_0$  the interception coefficient,  $\beta_i$  the linear terms,  $\beta_{ii}$  the quadratic terms,  $\beta_{ij}$  the interaction terms,  $x_i$  and  $x_j$  the coded values of the independent variables.

The Fisher's test for analysis of variance (ANOVA), effected on experimental data make it possible to estimate the statistical significance of the proposed models. Response surfaces as represented by Fig. 6 are drawn by using the *analysis design* procedure of *Statgraphics Plus for Windows* software (5.1 version).

## RESULTS AND DISCUSSION

The experiments of steam distillation were aimed at comparing the compounds extracted by this conventional process with those extracted by using a new method, such as the DIC process. Table 2 makes it possible to compare the compositions of the oil obtained from the two processes. When applying a processing pressure of 6 bar and a processing time of 8 minutes for the DIC treatment, the same compounds were found in the two processes but not in the same proportions. It appears that several compounds of low molecular weight (from  $\beta$ -pinene to camphol) are only found as trace for extractions by steam distillation while they are quantified for extractions by the D.I.C process. In contrast, the amounts in the heavier compounds are found similar.

In Table 3 are listed the values of coded variables and of the 5 responses corresponding to the yield in extracted oil and in the 4 selected compounds, for all the 12 experiments required by the experimental design procedure

The yields in extracted oil and in the 4 selected compounds were found to be strongly dependent on both the processing time and the processing pressure. The maximal yields in extracted oil (0.91 g/100 g), in plicatic acid, and 3-isopropylphenol (17.62 and 0.44 g/10<sup>4</sup> g respectively) were obtained at the highest processing pressure (6 bar) and the highest processing time (300 s). The maximal yields in carvacrol and myrtenol were reached at the highest processing pressure and intermediate processing time. In the regression analysis all the 5 responses were taken together into account.

**Table 2.** Composition of Red Cedar Wood Extract Obtained by Steam Distillation (SD) and by Instantaneous Controlled Pressure Drop Process (DIC).

	SD	DIC
$\beta$ -pinene	t	0.16
$\gamma$ -butylene	t	t
Fenchol	t	0.18
l-pinocarveol	t	0.36
isopinocampone	t	0.18
isocamphol	t	0.13
(s)-cis-verbenol	t	0.42
Camphol	t	0.32
p-cymen-8-ol	1.87	2.36
4-terpineol	2.85	5.95
o-cumenol	0.31	0.59
$\alpha$ -terpinenol	2.58	6.01
myrtenol	5.96	7.69
eucarvone	0.71	0.76
3-isopropylphenol	8.26	9.58
o-cymol	0.25	0.24
tert-butylquinone	0.25	1.87
Cuminal	0.55	0.6
Thymoquinone	3.58	2.39
2-carene-10-al	1.68	1.18
Carvenone	t	t
(-)-cis-myrtanol	0.63	0.26
carvacrol	0.44	0.56
linoleic acid	t	t
Terpin	0.29	0.11
methyl-cuminol	8.82	5.48
Eugenol	1.15	1.58
carbofuran phenol	7.74	4.54
plicatic acid	10.15	11.17
Cumol	4.42	5.2
tert-butylquinone	1.05	2.32
$\beta$ -eudesmol	1.17	1.3
3-tert-butyl-4-methoxyphenol	t	0.12
isoeugenol	0.21	t

*t* = trace

**Table 3.** Experimental Design and Results of E.O Yield and Extraction Yield of the Different Compounds

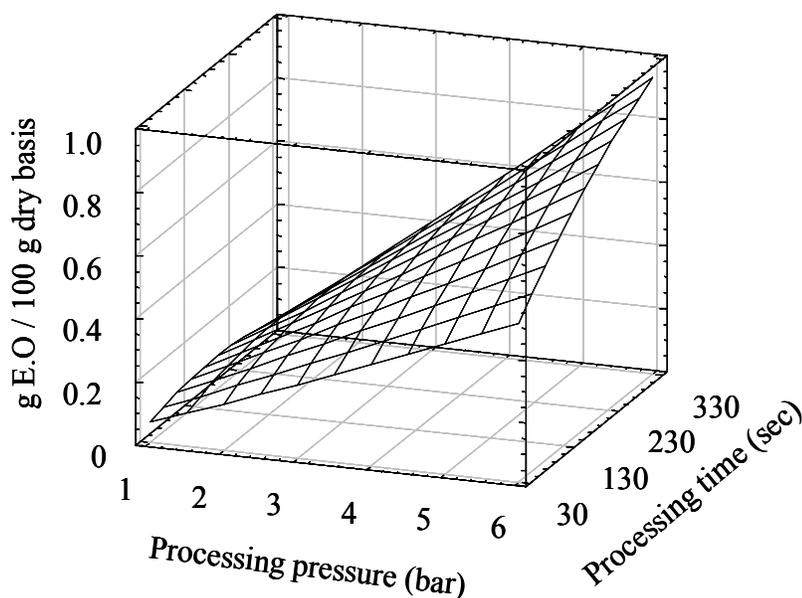
Runs	Levels of Independent variables		Responses				
	$x_1$	$x_2$	Extracted oil (E.O)	Plicatic acid	3- isopropylphenol	carvacrol	myrtenol
1	-1	+1	0.06	0.38	0.06	0.35	0.22
2	+1	-1	0.54	9.23	0.28	1.66	1.04
3	0	-1	0.33	6.45	0.22	0.93	0.72
4	-1	-1	0.08	1.49	0.07	0.45	0.09
5	+1	0	0.83	10.90	0.44	1.79	1.83
6	0	0	0.39	6.99	0.31	1.50	0.76
7	0	0	0.37	7.94	0.17	1.14	0.85
8	0	0	0.38	5.05	0.22	1.52	0.87
9	0	0	0.44	6.22	0.28	1.33	1.09
10	-1	0	0.10	0.41	0.09	1.46	0.43
11	0	+1	0.54	10.34	0.32	1.55	1.23
12	+1	+1	0.91	17.62	0.43	1.53	1.43
Mean absolute error for replications			3.02 %	1.05 %	0.10 %	0.15 %	0.12 %

$x_1$  = coded value of processing pressure (P),  $x_2$  = coded value of processing time (t), y: global oil yield.. The E.O yield is expressed in g/100 g dm and the different compounds are expressed in g/10<sup>4</sup> g dm.

### Effects of Steam Pressure and Processing Time on Extraction Yield

The results of the regression analysis i.e. the values of coefficients in the equation 2 are listed in Table 4. For the yield in extracted oil, the linear terms related to the processing pressure and to the processing time were statistically significant. The strong effect of the processing pressure is proven by the low p-value ( $p < 0.05$ ). P-value indicates the statistical significance of each parameter. It is based on hypothesis that a parameter is not significant, thus the closer this probability is to 0, the more an effect is significant. This is also obvious when considering Fig. 3, which shows the tri-dimensional response surface for the yield in extracted oil.

For a processing time fixed at its central value (165 sec), the E.O yield increased from 0.09 to 0.78 g/100 g when the processing pressure increased from 1 to 6 bar. On the other hand, when the processing pressure was fixed at a central value (3.5 bar), the change in the E.O yield was only from 0.30 to 0.49 g/100 g when the processing time increased from 30 to 300 s. This is probably the result of two simultaneous effects: a free diffusion phenomenon on the wood surface and a mechanical strain resulting from the drop of steam pressure with a subsequent degradation of wood cells.



**Fig. 3:** Response surface of the E.O yield as a simultaneous function of processing pressure and processing time

This degradation therefore involves the liberation of compounds initially located in the intact cells. The same observation was made by Spiro and Chen (1994), who reported that the essential oil synthesized in the secretory cells is not released unless an external factor damages the microstructure. The same authors (Chen and Spiro 1995) reported that a severe thermal stress such as irradiation with high microwave power, and the build-up within the cells, could have exceeded their capacity for expansion, thus causing them to break. These expansion phenomena were also observed by Nouviaire et al. (2001). Figure 3 also shows that the interaction between time and pressure was statistically significant ( $p < 0.05$ ). For a fixed processing pressure at its lowest level (1 bar), the yield in extracted oil was stable and equal to 0.07 g/100 g with a processing time increasing from 30 to 300 s. In contrast, with a processing pressure fixed at 6 bar, the yield in extracted oil varied from 0.55 to 0.94 g/100 g when processing times increased from 30 to 300 s. The F-test results of variance analysis for E.O yield listed in Table 5 revealed that the regression associated to the interaction between processing time and steam pressure was statistically significant ( $p < 0.05$ ). The regression coefficient of the model  $R^2$  was 0.98. The predicted model seemed to reasonably fit to experimental values, since the fitted model could explain 98 % of total variation.

### Yield in Oil as a Function of the Number of Expansion Cycles

To evaluate the effect of the mechanical strain induced by the brutal expansion in the DIC extraction, some experiments were performed by varying the number of cycles for given values of the processing time. The total processing time does not have the same importance according to the number of decompression cycles.

**Table 4.** Regression Coefficient of the Second Order Polynomial Equations (with coded variables) for the E.O Yield and for the Four Studied Compounds

Coefficients	E.O yield	Plicatic acid	3- isopropylphenol	carvacrol	myrtenol
$\beta_0$	0.414	0.066	0.003	0.014	0.010
$\beta_1$	0.678 <sup>a</sup>	0.118 <sup>a</sup>	0.003 <sup>a</sup>	0.009 <sup>a</sup>	0.012 <sup>a</sup>
$\beta_2$	0.184 <sup>a</sup>	0.037 <sup>a</sup>	0.001	0.002	0.003 <sup>b</sup>
$\beta_{11}$	0.032	-0.021	0	0	-0.002
$\beta_{22}$	- 0.029	0.034 <sup>a</sup>	0	- 0.008	-0.003
$\beta_{12}$	0.197 <sup>a</sup>	0.048 <sup>a</sup>	0.001	0	0.001

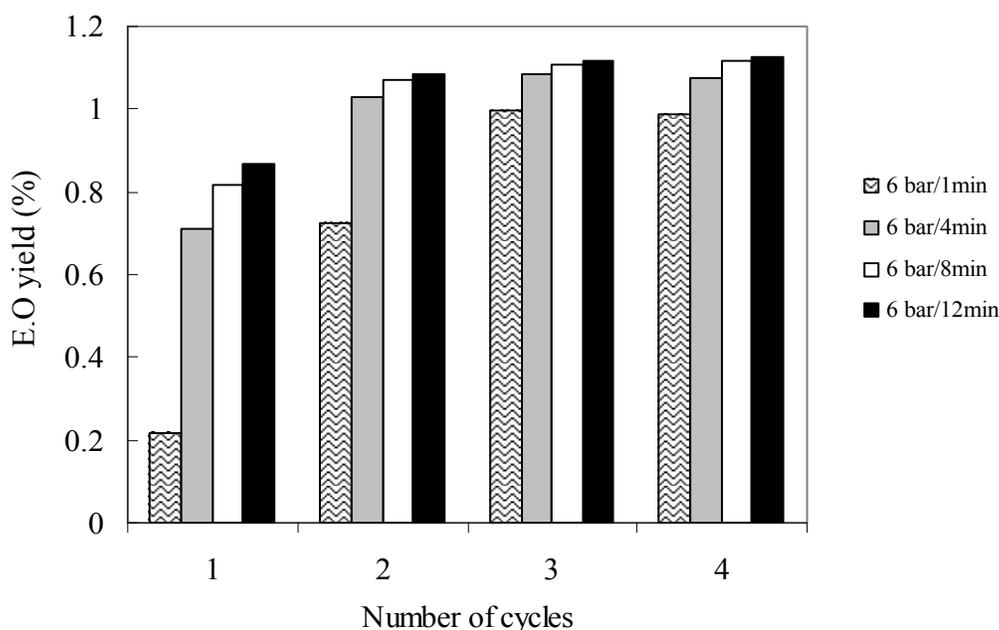
$\beta_0$  is the interception coefficient,  $\beta_i$  the linear terms,  $\beta_{ii}$  the quadratic terms,  $\beta_{ij}$  the interaction terms in eq (2); a : p-value < 0.05 ; b : p-value < 0.1

**Table 5:** Analysis of Variance Showing the Effect of the Processing Variables as a Linear Term, Quadratic Term, and Interactions on the E.O Yield

E.O yield				
Source	Degrees of freedom	Sum of squares	Mean square	F-Ratio
Model	5	0.78103	0.15621	42.114 <sup>a</sup>
Linear	2	0.73930	0.36965	99.632 <sup>a</sup>
Quadratic	2	0.00293	0.00147	0.396
Cross product	1	0.03880	0.03880	10.451 <sup>a</sup>
Residual	7	0.02596	0.00371	-
Lack of fit	3	0.00526	0.00175	0.474
Pure error	4	0.02070	0.00520	-
$R^2$			0.98	

a: p-value < 0.05

In the case of only one cycle, increasing processing time from 1 to 12 min resulted in an increase of oil yield from 0.22 to 0.87 g/100 g. This gap was not so large when the number of cycles increased. For two D.I.C cycles, a processing time of 1 min (one pressure drop after 30 sec and one after 1 min) gave an extraction yield of 0.72 g/100 g, while a processing time of 12 minutes (two pressure drops after 6 and 12 minutes) gave an extraction yield of about 1.08 g/100 g. As shown by Fig. 4, this gap was even smaller for 3 and 4 D.I.C extraction cycles. With 3 cycles, 1 minute was enough to extract 1 g/100 g, while 12 min did not enable the recovery of more than 1.12 g/100 g. Above 3 D.I.C cycles, the extraction yield was not improved, and no differences were visible between the 3<sup>rd</sup> and the 4<sup>th</sup> cycle, indicating that the substrate was used up. To extract heat-sensitive compounds, it is better to operate at the shortest processing time, but with at least 3 expansion cycles.



**Fig. 4:** Effect of the number of decompressions (cycles) on the extract yield with different processing time. In these experiments the processing pressure was fixed at 6 bar.

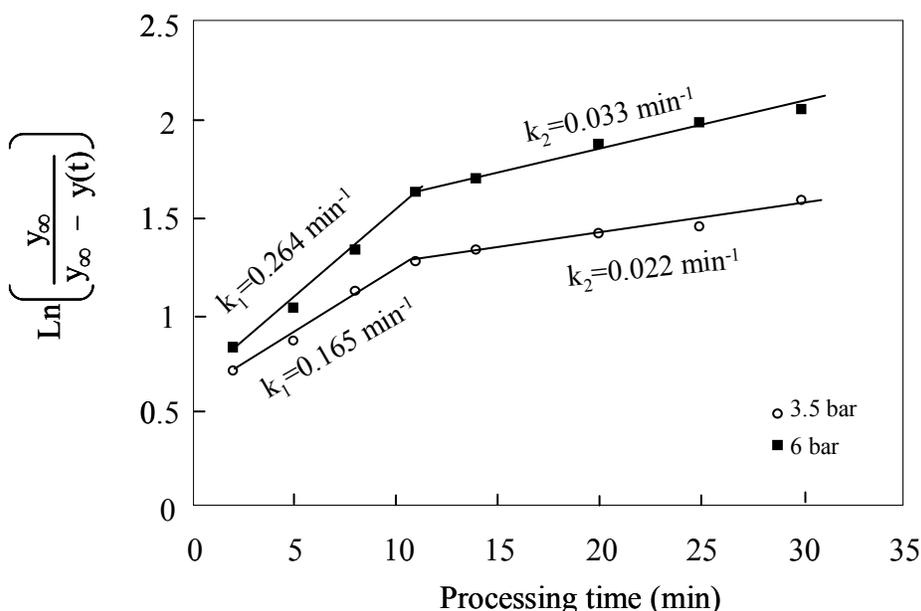
### Kinetics of Oil Extraction from Red Cedar Wood

As illustrated by Fig. 5, the change in oil yield versus time was fast during the first 5 minutes of the DIC process and much slower after this period before reaching an equilibrium value. The rate of oil extraction was assumed to obey a first order kinetic law, an assumption supported by various authors such as Spiro and Selwood (1984). In integrated form, the kinetics are described by equation 3,

$$\ln\left(\frac{y_{\infty}}{y_{\infty}-y(t)}\right) = k_i t + a \quad (3)$$

where  $y_{\infty}$  is the extraction yield at the end of process,  $y(t)$  the yield of extraction at time  $t$ ,  $k_i$  a first-order rate constant, and  $a$  the semi empirical intercept.

It is clear from Fig. 5 that the extraction of oil occurred in two distinct kinetic steps, a fast step followed by a slower one, as testified by the rupture of slope in the linear plots drawn in Fig 5. Each step was characterised by its own value of the kinetic constant. Whatever the processing pressure applied, 3.5 or 6 bar, the amount of oil recovered in the second step (around 9 %) was much smaller than that recovered during the first step (around 91%). It can be supposed that the major part of the recovered oil in the first step was constituted by light compounds easily extractible by evaporation or by free diffusion.



**Fig. 5.** First-order plots for the two stages of oil isolation from red cedar wood by the D.I.C process for two processing pressures: 3.5 and 6 bar.

### Effects of Processing Conditions on the Four Selected Compounds

From Fig. 6(1), it is clear that the processing pressure had the strongest effect on the yield in plicatic acid. It varied from 0.38 to 17.9 g/10<sup>4</sup> g when processing pressure increased from its low level (1 bar) to its high level (6 bar) and for a processing time maintained at “+1” level (300 s). However, this evolution was true only for the highest processing times.

For the lower processing time (30 s) and for the same variation in processing pressure, the extraction yield of plicatic acid varied only from 1.5 to 9.2 g/10<sup>4</sup> g. These results can be favorably compared to those of Štěrbová et al. (2004), who studied the effect of experimental conditions of microwave-assisted extraction (MAE) such as temperature. The MAE combined to a solid-phase purification were performed prior to the chromatographic determination of phenolic compounds such as benzoic acid (which is close to plicatic acid) in plant materials. These authors observed that the temperature substantially influenced amounts of recovered components. The maximum yield in the benzoic acid is obtained at 70°C. A negative influence on the amount of isolated phenolic compounds was observed when increasing temperature above 70°C, probably due to their degradation.

In this study, in spite of a high temperature corresponding to 6 bar steam pressure, i.e., above 160°C, no degradation was observed. This may be due to the low processing time associated to this high temperature. The processing time was 5 minutes at the maximum, compared with at least 20 minutes for microwave-assisted extraction. From a statistical point of view, the processing time also had a significant effect on the plicatic acid yield, which changed from 6 to 11 g/10<sup>4</sup> g, for a processing pressure fixed at its central level (3.5 bar) (Fig. 6(1)). This indicates that extraction of plicatic acid is more

sensitive to the mechanical effect of a sudden drop in pressure than to diffusion effect induced by steam in contact with wood particles. Increasing processing pressure also had a strong effect on 3-isopropylphenol yield (Fig. 6(2)). When it varied from 1 to 6 bar and for a fixed processing time (165 sec), the yield of 3-isopropylphenol increased from 0.08 to 0.4 g/10<sup>4</sup> g. For this compound, the effect of processing time was less important and statistically not significant. For a processing pressure fixed at its central value, a change of processing time from its low level (30 sec) to its high level (300 s) led to an increase of 3-isopropylphenol only from 0.20 to 0.28 g/10<sup>4</sup> g. Fung and Long (2001) also reported a positive effect of a higher pressure in supercritical fluid for extraction of phenols as 3-isopropylphenol. However, they concluded that an increase in temperature lowers the recovery of 3-isopropylphenol.

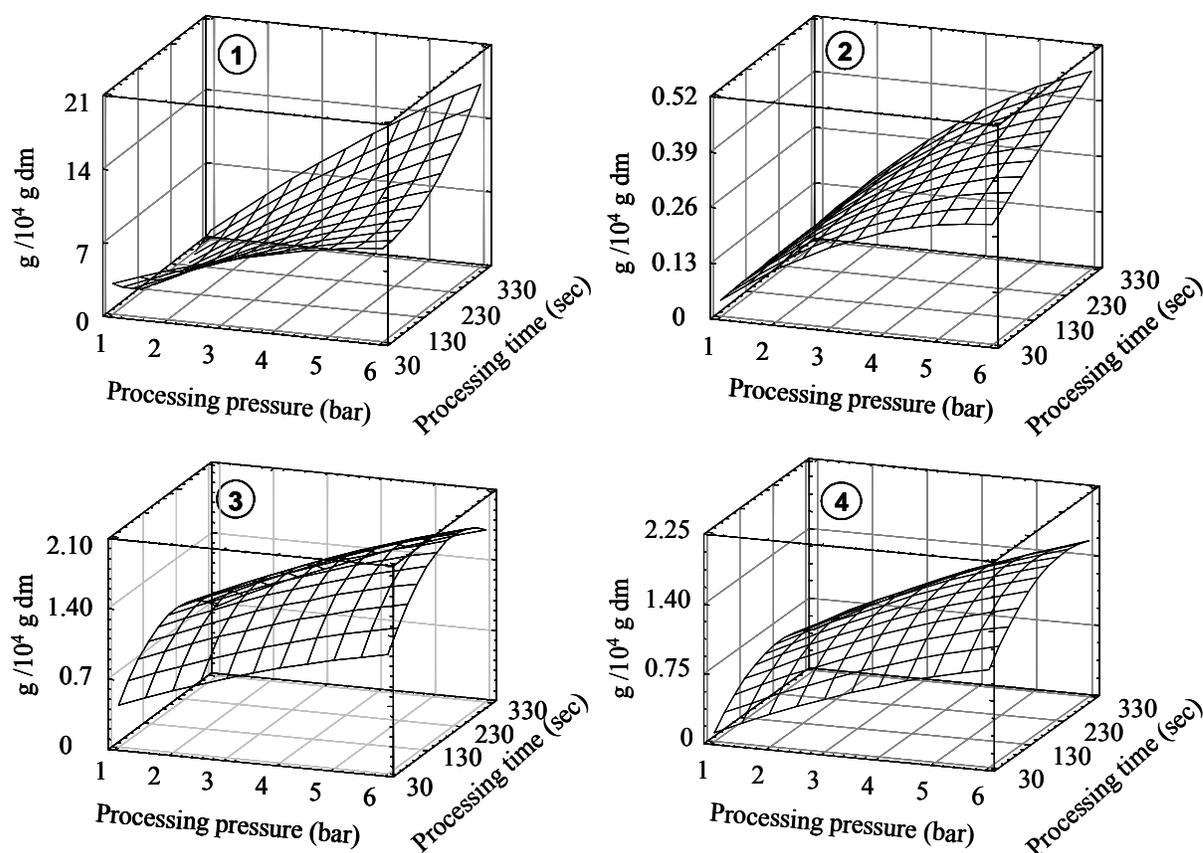


Fig. 6: Response surface of the mass in the different oil compounds extracted as a simultaneous function of processing pressure and processing time. (1) plicatic acid; (2) 3- isopropylphenol; (3) carvacrol; (4) myrtenol.

The third compound considered in this study (carvacrol) showed a different behavior compared to the first two (Fig. 6(3)). The processing pressure and the quadratic effect of the processing time were statistically significant. Whatever the processing

pressure, the yield in carvacrol increased up to a maximal value and then it decreased, thus indicating a degradation of this compound when the processing time was over 200 s.

From Fig. 6(4) it can be seen that the variation of myrtenol yield was similar to that of 3-isopropylphenol. Whatever the processing time, the processing pressure had a strong effect on the yield in myrtenol. In contrast, the processing time was statistically not significant ( $p < 0.05$ ). By fixing the processing time at its central value (165 sec), the yield in myrtenol increased from  $0.4 \text{ g}/10^4 \text{ g}$  to  $1.6 \text{ g}/10^4 \text{ g}$  when the processing pressure varied from 1 to 6 bar. On the other hand, by keeping the processing pressure at its central value (3.5 bar), it increased only from 0.69 to  $1.03 \text{ g}/10^4 \text{ g}$  when the processing time varied from 30 to 300 seconds. A weak quadratic effect can be observed (Fig. 6(4)), but it was statistically not significant. A strong effect of processing pressure was also observed in a previous work (Rezzoug et al., 2005) for alcoholic compounds such as  $\alpha$ -terpineol. The alcohols were not as easily extractible as the terpene hydrocarbons. We supposed that a large part of alcoholic compounds are not located on the surface of naturally broken cells as terpene hydrocarbons.

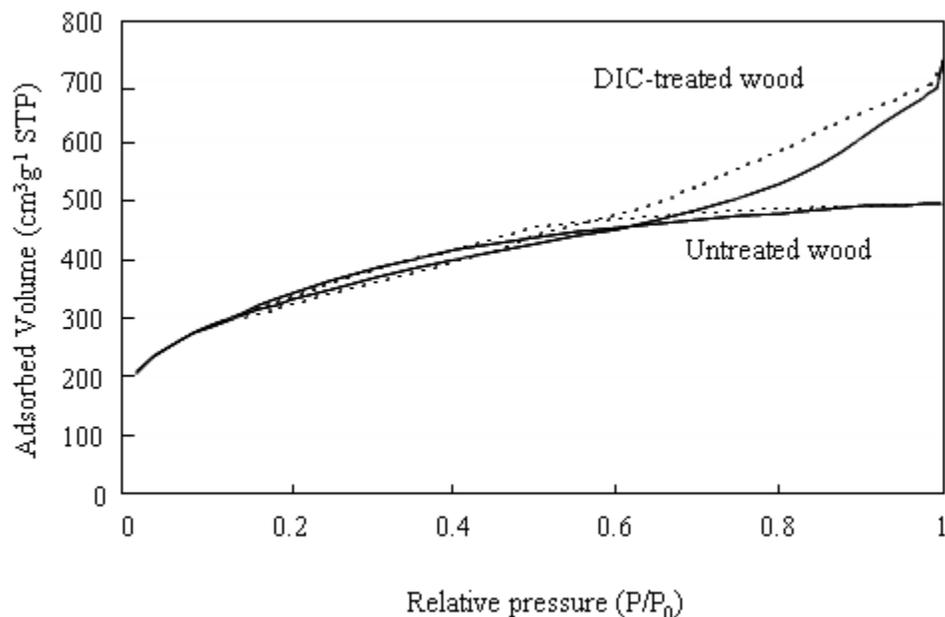
### Effects of DIC Treatment on the Quality of Activated Carbon from Residual Wood

According to Hu et al., (2008), the expansion at the end of pretreatment by steam explosion process opens up the particulate structure of wood and the removal of hemicelluloses improves the accessibility of cellulose to enzymes. In this study we used this phenomenon to improve the porosity, which is a critical qualitative criterion of activated carbon produced in the second step of the process. The activated carbon from untreated and DIC-treated wood (at 8 bar and 3 min of processing time) were well characterized by their adsorption isotherms of  $\text{N}_2$  at 77K, as shown by Fig.7. The activated carbon from untreated wood exhibited a sorption isotherm of type I, according to the IUPAC nomenclature, thus indicating a structure of carbon that was essentially micro-porous. On the contrary, the adsorption isotherm of activated carbon from DIC-treated wood belongs to the type IV and exhibit a neat hysteresis. This hysteresis, which occurs at high values of relative pressure  $P/P_0$  is related to the filling of the mesopores (2-50 nm) by capillary condensation.

The DIC-treatment thus enhanced the formation of mesopores to the detriment of micro-pores within the char. Table 6 shows large differences between DIC-treated and untreated wood with respect to the mean diameter of pores and the total volume of micropores. Indeed, for the A.C. from DIC-treated wood, the mean diameter was significantly higher, while the volume of micropores was much lower. On the contrary, for the BET surface area, no marked difference was observed between treated and untreated wood. The presence of larger pores in the A.C. from DIC-treated wood was certainly due to the excessive expansion of wood during its pre-treatment.

**Table 6:** Adsorption of  $\text{N}_2$  at 77K on Activated Carbons

Precursor	Surface BET $\text{m}^2\text{g}^{-1}$	Micropores volume ( $\text{cm}^3\text{g}^{-1}$ )	Total volume of pores ( $\text{cm}^3\text{g}^{-1}$ )	Mean diameter of pores $\text{Å}$
Untreated wood	1172	0.134	0.758	24.66
DIC-treated wood	1178	0.012	1.036	35.17



**Fig.7:** Adsorption-desorption isotherms of N<sub>2</sub> at 77K on phosphoric-activated carbons prepared from untreated and DIC-treated wood

## CONCLUSIONS

1. A 3<sup>2</sup> full-factorial design method was used to determine the optimum conditions of oil extraction from red cedar wood by a recent technique, the instantaneous controlled pressure drop process (DIC). Five responses were investigated, the global extraction yield and the yield of four compounds of oil namely: plicatic acid; 3-isopropylphenol; carvacrol and myrtenol. From the experimental results, the optimum conditions for the global extraction yield, for plicatic acid, and for 3-isopropylphenol were: 6 bar for processing pressure and 300 seconds for processing time. For carvacrol and myrtenol, the optimal processing pressure was also 6 bar, but the optimal processing times were respectively 175 s and 227 s, indicating a certain degradation of these two compounds.
2. According to the statistical method, a second order polynomial function is assumed to mimic the global extraction yield and the extraction yield of the oil compounds. The adequacy test of the models, estimated by the coefficient of determination R<sup>2</sup> given in Table 5, revealed that they are quite adequate with a probability of rejecting the lack of fit greater than 0.05.
3. The number of pressure drops was also investigated. It appears that a high extraction yield (~ 1g /100 g) can be obtained by reducing the processing time from 300 sec to 60 sec and by increasing the number of pressure drops from 1 to 3. It should be noted that for traditional extraction processes, only 0.5 to 0.8 g /100 g as extraction yield is generally obtained.

4. One can also conclude that there is a beneficial effect of the DIC-treatment for producing A.C., since it results in a larger staggering of pores size. The produced A.C. is not too selective and able to adsorb polluting compounds in a large scale of sizes.

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